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Shear-induced crystallization in a blend of isotactic polypropylene and high density polyethylene

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ABSTRACT

Shish–kebab morphologies were observed with relatively low shear rate and low temperature in the phase-separated isotactic polypropylene (iPP) and high density polyethylene (HDPE) blend. Both components are crystallizable polymers. In our experiments, relatively low shear rates and low temperatures were used, so that the entangled network chains cannot be broken up or disentangled, and the shish nuclei must be formed from oriented and stretched network chains instead of a bundle of pulled-out chains. The effects of shear rate, shear time and temperature on the formation and morphology of shish–kebabs were studied by in situ optical microscopy and shear hot stage under various thermal and shear histories. Optical microscopic measurement showed that the length of iPP cylindrites is much longer than the dimension of phase domains, which implies that iPP cylindrites grow through both iPP and HDPE phase domains. An unexpected 'core–shell' structure was observed in the melting procedure, which could be explained by the difference of crystallinity between 'core' and 'shell'. It is most important that two kinds of shish–kebabs, the interface morphology and transcrystallites were observed by scanning electron microscopy (SEM). SEM observation also revealed that the width of iPP shish is about 1–2 μm and the width of HDPE shish is about 100 nm. The difference in the shish width probably resulted from the lower molecular weight, higher polydispersity, less inter-chain interaction force, and faster nucleation and growth rate of HDPE relative to the iPP chains.

1. Introduction

Polymer melts under shear can exhibit many important macroscopic effects including flow-dependent viscosity, higher normal stresses, enhanced nucleation and crystallization rate, and shish–kebab (cylindrite) morphology formation. The study of the crystallization process of polyolefin from melt under shear can provide fundamental knowledge in order to control the morphologies and properties of products obtained from various processing conditions. This kind of understanding into the molecular conformations, ordering processes, and nucleation and crystallization kinetics has drawn a lot of interests recently [1–10].

Hsiao and coworkers [11] studied shish–kebab structures of iPP and ultrahigh molecular weight polyethylene (UHMWPE) with wide-angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS) and scanning electron microscopy (SEM). They have proposed that stretched chain or stretched chain segments form shish. They have also suggested that the nature of shish could be amorphous, mesomorphic or crystalline. Meanwhile, they [12,13] found that the formation of iPP shish–kebab structure could be facilitated by the presence of oriented UHMWPE domains, because interfacial frictions could impede the relaxation of iPP chains. Besides, Hsiao agreed with Keller's view that long chains play a vital role in the formation of shish. On the other hand, Kornfield and coworkers [14] studied the shish–kebab morphology of iPP with transmission electron microscopy (TEM), SAXS and small angle neutron scattering (SANS), and they reported that the concentration of long chains in shish was not higher than that in the whole material. This result indicated that the longest, most extended chains may not be predominant in shish. Qiang Fu and coworkers [15] obtained shish–kebabs in the blends of iPP and HDPE by using dynamic packing injection molding. They used SAXS, wide-angle X-ray scattering (WAXS), differential scanning calorimetry (DSC) and optical microscopy to investigate shish and re-crystallization behavior of iPP/HDPE blends, and found that shish size increased with the increase of HDPE concentration. In another experiment,

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they mixed polypropylene (PP) and linear low density polyethylene (LLDPE), and sheared the blend also with the method of dynamic packing injection molding. They reported that PP shish–kebabs could be achieved in all three layers – skin layer, oriented layer and core layer. In contrast, in LLDPE phase, part of LLDPE lamellae stacks was oriented perpendicularly to the shear direction and the other lamellae stacks were oriented 45–50° away from shear direction [16].

Studies on the shear-induced crystallization of polyolefin have also been carried out by Han and coworkers recently. In situ polarized optical microscopy [17], in situ small angle light scattering (SALS), and ex-situ atomic force microscopy (AFM) [18] were used to investigate the melt state shear-induced crystallization behavior of iPP at low shear rate and low temperature. The process of iPP cylindrite growth, microstructure of cylindrite especially the shish-like core, length changes of shish-like core, and β-form of iPP crystallization have been studied. Another research subject of Han and coworkers recently was shear-induced crystallization of phase-separated blend of iPP and elastomer poly(ethylene-*co*-octene) (PEOc) using in situ optical microscopy [19,20]. It was shown that shish–kebab morphology could be formed at low shear rate not only in pure iPP, but also in iPP and PEOc blend. It was demonstrated that shear rate and shear time had very important effects on the formation and the total quantity of cylindrites. At low shear rate, three types of shish–kebab structures were observed, indicating that the shish nuclei are initiated from the entangled chains. The kebab grows epitaxially in the direction perpendicular to the narrow backbone or shear direction.

Previous studies including Hsiao's [11–13], Kornfield's [14], Fu's [15,16], Kanaya's [21,22] and ours [17–20], indicate that the mechanism of shish–kebab formation in bulk is not the same as that in the solution. We have carried out experiments on two components system before to demonstrate the nucleation under shear is due to deformed network strands [19,20]. In this paper we present again two components and liquid–liquid phase separated (LLPS) system. However, this system involves two crystallizable components. LLPS as well as two different crystallization kinetics and morphology are involved. In addition, it is well known that there is interplay between LLPS and crystallization of polymer blends, and iPP and HDPE can form shish–kebab structure with suitable shear condition in their pure state, separately. This paper is also designed to evaluate the influence of interplay between LLPS and crystallization on shish–kebab formation. Our results indicate that at higher isothermal crystallization temperature where iPP was a crystallizable component while HDPE was not easily crystallizable or even noncrystallizable under weak shear condition, it was found that the iPP shish–kebab structure could be formed in this phase-separated blend. After the blend isothermally crystallized at higher temperature for an extended time, we then lowered the temperature, so that HDPE could crystallize at a rapid rate, and then two kinds of shish–kebabs could be observed in the blend. One was shish–kebab structure of iPP, and the other was HDPE shish–kebab. It is the first time that two kinds of shish–kebabs are obtained in a polymer blend with two crystallizable polyolefin components, which has provided some new understandings on the formation and the morphology of shish–kebab structures.

2. Experimental section

2.1. Materials

Both the iPP ($M_w = 3.0 \times 10^5$, polydispersity $M_w/M_n = 3.9$) and HDPE ($M_w = 2.0 \times 10^5$, polydispersity $M_w/M_n = 7.4$) were provided by Yanshan Petrochemical Corp., Inc.

The iPP/HDPE blends used in this experiment were prepared via solution coprecipitation method. These two components were first dissolved in xylene solution at 130 °C for 24 h. Then the solution was poured into cooled methanol to precipitate the polymer mixture. After filtration, this mixture was washed with clean methanol for several times and dried in a vacuum oven at 45 °C for 72 h.

2.2. Shear apparatus

A Linkam CSS-450 shearing hot stage (Linkam Scientific Instruments Ltd, Tadworth, Surrey, UK) was used to control thermal history of the samples, as well as the shear field. The adjustable parameters by using this hot stage include sample thickness, temperature, shear rate, and heating/cooling rate.

2.3. Optical microscopy

The optical microscopy observation was carried out by using an optical microscope (Nikon ECLIPSE E600POL) and a digital camera (NikonCOOLPIX4500).

2.4. SEM

The blend sample was obtained from the shear hot stage after the optical microscopy measurements and etched for 1 h by potassium permanganate solution of concentrated sulphuric acid and orthophosphoric acid [23–25]. Then the surface was platinum coated for SEM measurements. The highlighted crystalline structure was observed with a scanning electron microscope (JSM – 6700F, JEOL), operating at 10 kv.

2.5. Experimental procedure

Fig. 1 shows the thermal history and shear conditions in this experiment. Samples were heated to 200 °C and held there for 10 min to eliminate thermal history. Liquid–liquid phase separation also happened in this procedure.

3. Results and discussion

3.1. Shish–kebab morphologies of iPP, HDPE, and their blends

iPP, HDPE, and iPP/HDPE = 50/50 (wt%) blend are subjected to the same thermal history and shear conditions as indicated in Fig. 1. Fig. 2(A) and (B) is the polarized optical micrographs of crystallization process of pure iPP and HDPE samples under shear respectively, in which the micron sized fibril-like supermolecular cylindrites or shish–kebab morphologies can be clearly observed. Two different kinds of shish–kebab structures which grow along the epitaxial direction with time and perpendicularly to the narrow

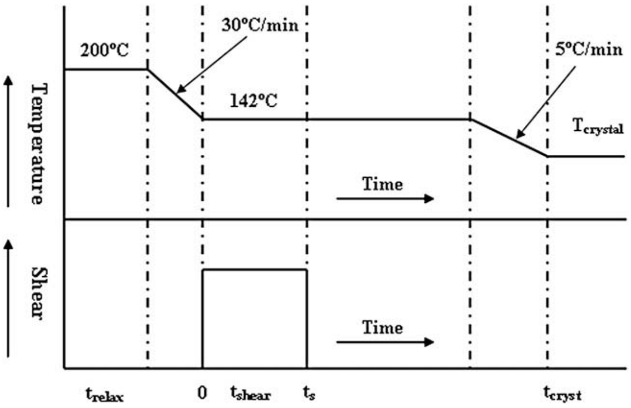


Fig. 1. Schematic diagram of the temperature and shear conditions as a function of time during shear experiments.

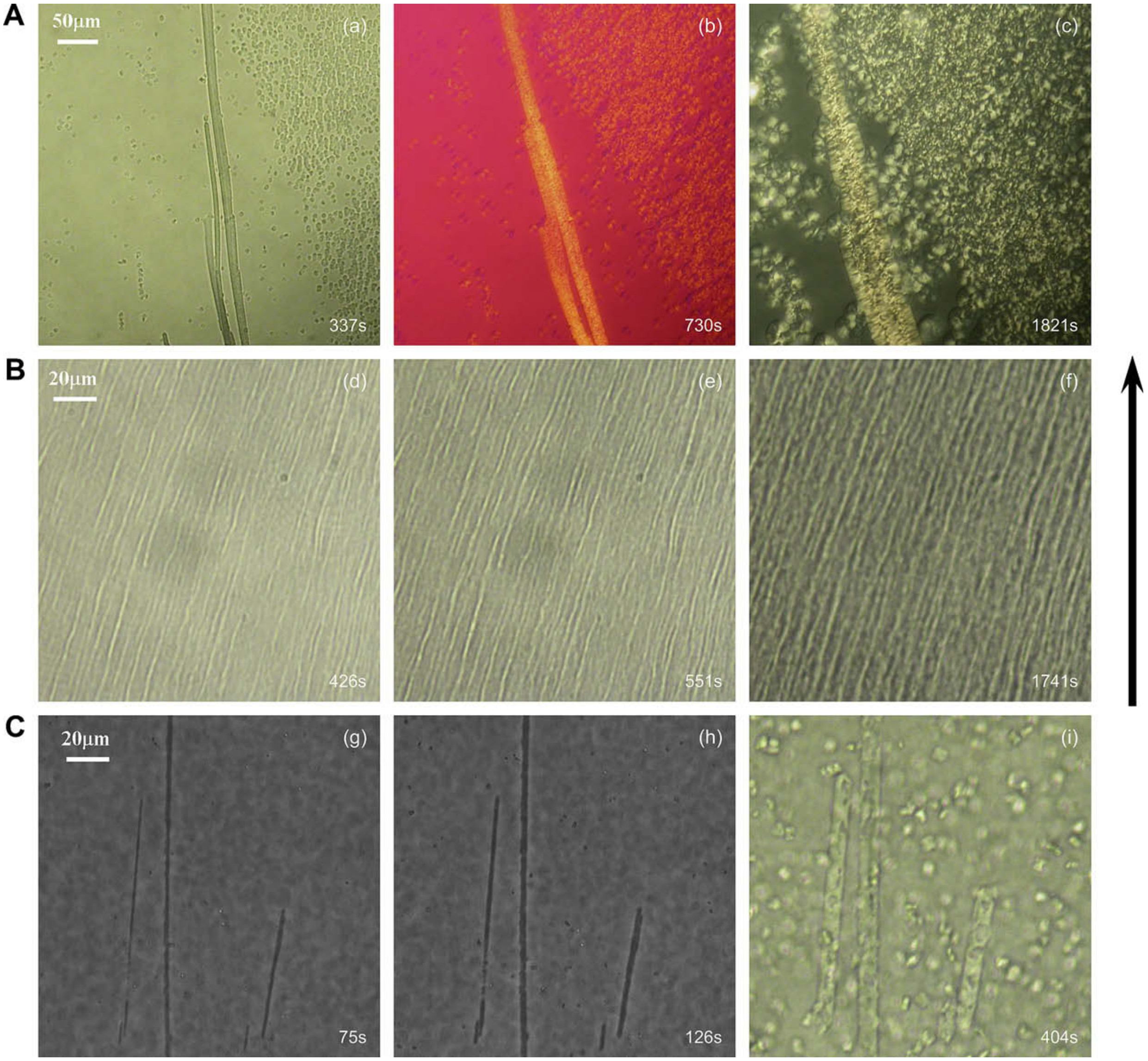


Fig. 2. Optical micrographs of iPP, HDPE and iPP/HDPE = 50/50 samples: (A) polarized optical micrographs of iPP sample sheared at 142 °C with shear rate 3 s^{-1} and shear time 30 s, then isothermally crystallized at 142 °C for different time periods (0 s is correspondent to the shear cessation). (B) Polarized optical micrographs of HDPE sample sheared with shear rate 6 s^{-1} and shear time 60 s at 142 °C, then cooled to 123 °C at the rate of 5 °C/min and isothermally crystallized at 123 °C for different time periods. (C) Optical micrographs of iPP/HDPE = 50/50 sample sheared at 142 °C with shear rate 3 s^{-1} and shear time 30 s, then isothermally crystallized at 142 °C for different time periods. (a), (d), (e), (f) and (i) are polarized optical micrographs taken by means of 1/4λ plate; (b) is polarized optical micrograph taken by means of λ plate; (c) is polarized optical micrograph; (g) and (h) are phase contrast micrographs. The arrowhead represents shear direction and the crystallization time is indicated in the figures.

backbone or shear direction can be observed. The lateral growth of iPP shish–kebabs is much more obvious than that of HDPE shish–kebabs, and the final width of iPP shish–kebab is much larger. The width of iPP shish–kebab is about 10 μm after iPP isothermally crystallized at 142 °C for 337 s (cf. Fig. 2(a)), and it turns to be larger than 25 μm after iPP isothermally crystallized at 142 °C for 1821 s (c). Compared with iPP, the width of HDPE shish–kebab seems nearly unchanged during the whole crystallization process at 123 °C. Fig. 2(d) shows the width of HDPE shish–kebab is around 1–2 μm after HDPE isothermally crystallized at 123 °C for 426 s, and it is still around 1–2 μm after isothermal crystallization of HDPE at 123 °C for 1741 s as shown in (f). We could see that the final width of HDPE shish–kebab is in consistence with many other reports in the literature [10,26]. So it is very easy to distinguish iPP shish–kebab and HDPE shish–kebab in the phase-separated blend of iPP and HDPE by their width.

The width difference of the shish–kebabs of iPP and HDPE arises from their different chain structures. HDPE chains without methyl side groups have better regularity than iPP chains, so they are easier to be packed into lattice to form crystals. This feature of HDPE chain structure leads to higher nucleation density and growth rate than that of iPP at similar supercooling from their melting temperature. Thus the spherulites and shish–kebabs of HDPE can only grow into limited size because of the large number of simultaneously growing crystals. Due to its relatively low nucleation density and growth rate, iPP crystals have more space and time to grow into a bigger size before impinging onto another crystal.

The observation with optical micrograph by Meng et al. [19,20] showed that cylindrite length could exceed the size of liquid–liquid phase separation domains in iPP/PEOc blend, and similar phenomenon was observed in this blend system of iPP and HDPE. When the crystallization temperature in this experiment was chosen at 142 °C, iPP is crystallizable while HDPE is not easily crystallizable or even noncrystallizable under weak shear condition. Fig. 2(C) is phase contrast micrographs of iPP/HDPE = 50/50 blend sheared and then isothermally crystallized at 142 °C for different time periods as indicated in the figures. In Fig. 2(g), long and straight supermolecular structures (cylindrites or shish–kebab morphologies) are observed after shear cessation, which are in resemblance to the polymeric 'shish–kebab' morphology in pure iPP or iPP/PEOc blend [17–20]. Firstly, the cylindrites are much longer than the dimensions of liquid–liquid phase-separated domains of iPP/HDPE blend and seem to have passed through multiple phase domains, thus the nature of shish should be a bundle of elongated, orientated and entangled network strands. If shish is formed by fully extended chains, it would not grow through HDPE domains and the cylindrite would not be continuous through both phase domains. Secondly, the length of cylindrites in this study far exceeds that of a single chain, which verifies that shish should not be formed from some pulled-out and stretched single chains. Finally, the critical shear rate for network disentanglement or Newtonian to non-Newtonian transition is around 100 s^{-1}, which is much higher than the shear rate of cylindrite formation in our experiment. All these evidences have further corroborated the viewpoint and proposed model of Han and coworkers on the mechanism of shish–kebab structure in the melt [17–20].

During the crystallization process of iPP/HDPE blend system at 142 °C, it has been observed that there are some defects in the shish–kebab structure. This phenomenon was also observed in the iPP/PEOc blends studied by Han and coworkers recently [20]. The physical interpretation of this is that the shish can grow through iPP rich domains as well as the PEOc rich domains. When it passes through the PEOc rich domain, which is noncrystallizable, the growth of lamellae in the direction perpendicular to the shear direction (kebabs) is impossible [19,20]. Similarly, defects in cylindrites of iPP/HDPE blend could be also due to that HDPE chains could not stack lamellae along the epitaxial direction when the cylindrite grows through HDPE rich domains at this temperature.

Another interesting phenomenon is also observed in this study, which is the shape of some defects or the combination of some defects with respect to those neighboring cylindrites looks like that of a phase domain (cf. Fig. 3). This further implies that noncrystalline HDPE phase domains serve as defects in iPP shish–kebab structure of iPP/HDPE blend. It is understood that iPP cylindrites could grow through many iPP and HDPE rich domains along the cylindrite (or shear) direction. On the other hand, when one cylindrite passes through a certain noncrystalline HDPE phase domain, another adjacent cylindrite which is close enough to the former one could probably grow through the same noncrystalline HDPE phase domain. Hence, if these two defects in adjacent cylindrites are combined together, its shape must resemble to that of the HDPE rich domain.

3.2. Shear rate dependence and shear time dependence

Fig. 4(A) illustrates shish–kebab morphologies in iPP/HDPE = 50/50 blend with the same thermal history, gap, and shear time, but with different shear rates. When the shear rate is 4 s^{-1}, a straight shish–kebab structure extending through many different phase domains could be observed. When the shear rate is raised to 6 s^{-1}, more shish–kebabs could be seen, and more spherulites also appear. When the shear rate is further increased to 15 s^{-1}, it is apparent that lots of shish–kebabs are distorted due to the rotational nature of shear field. Fig. 4(B) shows the effect of shear time on the shish–kebab morphology. It is seen that the number of cylindrites is increased with the shear time increasing from 10 s to 60 s.

Based on the above observation, it could be deduced that shear rate is a more important parameter than shear time in shear-induced crystallization. When the shear rate exceeds the rate of network relaxation (the inverse of the relaxation time of the entangled network chains), the entangled network could be stretched and further developed into shish-like nuclei, and consequently the cylindrites are produced. The increase of shear time can increase the number of nuclei, because nucleation is a metastable process and increasing time can increase the overall probability for the system to overcome the free energy barrier and form nuclei.

3.3. "Core–shell" structure

By selecting appropriate experimental procedure, an interesting structure somewhat like "core–shell" structure could be obtained in iPP/HDPE = 50/50 blend. Fig. 5(a) shows the iPP/HDPE = 50/50 sample sheared with shear rate 1.5 s^{-1} and shear time 10 s and isothermally crystallized at 142 °C for 558 s. The molten polymer under shear can form the supermolecular structure – cylindrites or 'shish–kebab' morphologies. At this temperature, the HDPE component is difficult to crystallize under weak shear condition, so this kind of structures is mainly formed by iPP chains. Then the temperature was decreased to 124 °C at the rate of 5 °C/min, the shish–kebab structures grew wider and wider as shown in Fig. 5(b). During this cooling process, not only the iPP chains but also the HDPE polymer chains can crystallize because the temperature is

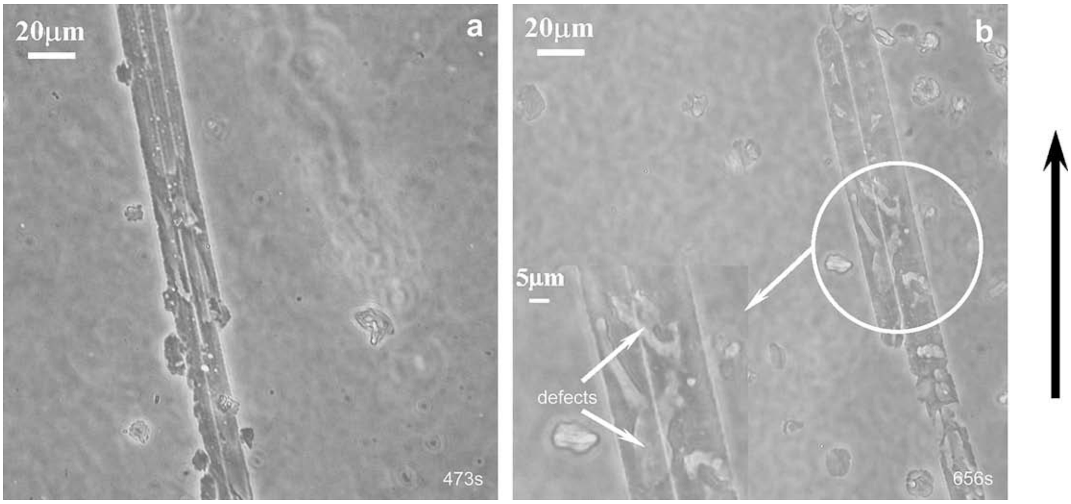


Fig. 3. Phase contrast micrographs of iPP/HDPE = 50/50 sample sheared at 142 °C with different shear rates and shear time periods, then isothermally crystallized at 142 °C for different time periods. (a) The shear rate is 5 s^{-1} and the shear time is 10 s; (b) 2 s^{-1} and 60 s. The arrowhead represents shear direction, and the crystallization time is indicated in the figures. The inset shows higher magnification optical micrograph of the circled defects.

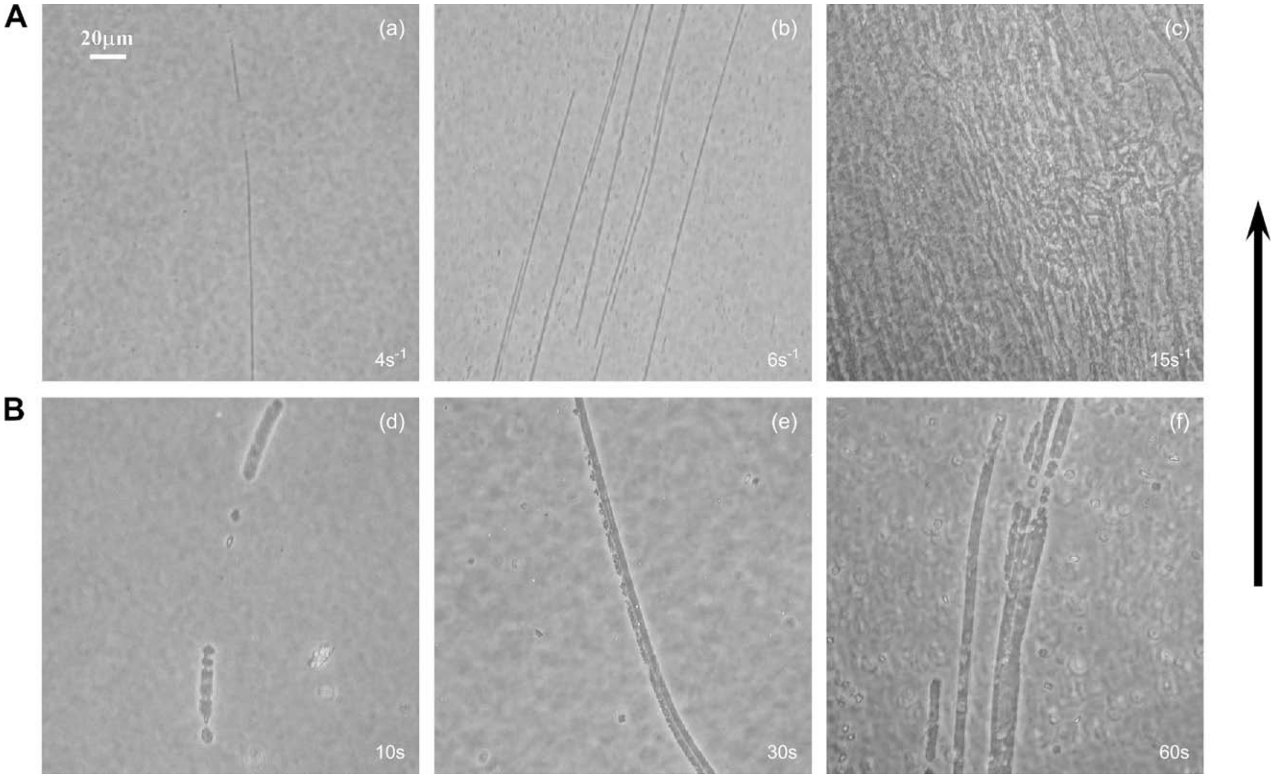


Fig. 4. Phase contrast optical micrographs of iPP/HDPE = 50/50 sample: (A) The sample sheared with different shear rates and isothermally crystallized at 142 °C for (a) 90 s, (b) 91 s, (c) 89 s. The shear time is 30 s and the shear rate is indicated in the figures. (B) The sample sheared with different shear time periods and isothermally crystallized at 142 °C for (d) 399 s, (e) 300 s, (f) 271 s. The shear rate is 1.5 s^{-1} and shear time is indicated in the figures. The arrowhead represents shear direction.

lower than the equilibrium melting point of polyethylene which is about 145 °C [27]. Since the growth rate of HDPE is faster than that of iPP, the HDPE polymer chains are involved in the crystallization at this stage and form the shell of cylindrites and some not yet crystallized iPP polymer chains could be pushed to the outside of the shell structures, so that the HDPE chains can crystallize and fill in the available space first. As soon as the temperature reached 124 °C (Fig. 5(b)), we increased the temperature back to 145 °C at the rate of 30 °C/min and held there for 10 min. Fig. 5(c) shows the morphology of cylindrites when the sample reached 145 °C, while (d) displays the morphology of cylindrites after the sample isothermally crystallized at 145 °C for 10 min. Finally, the temperature was increased to 170 °C at the rate of 2 °C/min to observe the melting process (Fig. 5(e)–(h)). When the temperature was elevated to the melting range of iPP crystals, a "core–shell" structure is clearly observed (Fig. 5(g)), which indicates that the melting temperature of the "core" is higher than that of the "shell". Meanwhile, the width of "core" is about the same as the width of the shish–kebabs which isothermally crystallized at 142 °C for 558 s (Fig. 5(a)). Therefore, we can conclude that the 'core' is the shish–kebab probably formed at 142 °C, and 'shell' are kebabs formed at lower temperatures. Moreover, a "sausage skin like layer" can also be observed in Fig. 5(g), we think this layer should be iPP crystals because the melting temperature of this structure is similar to that of iPP. Since HDPE can crystallize fast at 124 °C and fill in space, remaining iPP chains could have been pushed to the outside and form the "sausage skin like structure" when the temperature is held at 145 °C for 10 min.

3.4. Morphology and interphase structure by SEM

Fig. 6(a) and (b) shows the typical SEM images of the shear-induced structure from the iPP/HDPE = 50/50 blend. In Fig. 6(a), a long shish-like structure aligns along the shear direction. Parallel lamellae form the kebab structure, which grow from the central shish core and perpendicular to the shear direction. Fig. 6(b) is the shish structure from (a) at higher magnification. Some branching lamellae of the crystal structure are observed in Fig. 6(b) and this kind of structure can only be observed in iPP system [28,29]. Therefore, the crystalline structure in Fig. 6(a) and (b) should be attributed to the iPP cylindrite. Meanwhile, the average width of shish structure is about 1–2 μm, which is much larger than the radius of gyration of a macromolecule (20–30 nm). So there must be a lot of polymer chains involved in the process of forming the shish structure. Not only iPP cylindrites but also the iPP spherulites and the HDPE spherulites are observed as shown in Fig. 6(a) and (c). These spherulites may be formed at different stages or temperatures which cannot be identified at this time. Fig. 6(c) displays the interface between an iPP shish–kebab structure and HDPE spherulites. We can see that some lamellae of the iPP crystal stop growing at the interface and others extend from the iPP domain and penetrate into the HDPE domain. iPP kebabs and HDPE lamellae intertwined with each other. The system in this study is a phase-separated blend which has two-phase domains, of which one is the iPP rich domain and the other is the HDPE rich domain. But we should point out that some HDPE chains still exist in iPP rich domains and iPP chains in HDPE rich domains. So when the iPP lamellae grow through the domain interface and meet some crystallizable iPP polymer chains from the other domain on the interface, the iPP chains can continue to stack on to the lamellae of the iPP crystals, thus the iPP lamellae can penetrate into the HDPE phase domain. If the iPP lamellae meet many HDPE chains near the interface of HDPE rich domain, the growth of iPP lamellae becomes impossible.

Moreover, when two neighboring shish–kebabs are growing with time, lamellae from both sides can approach each other as

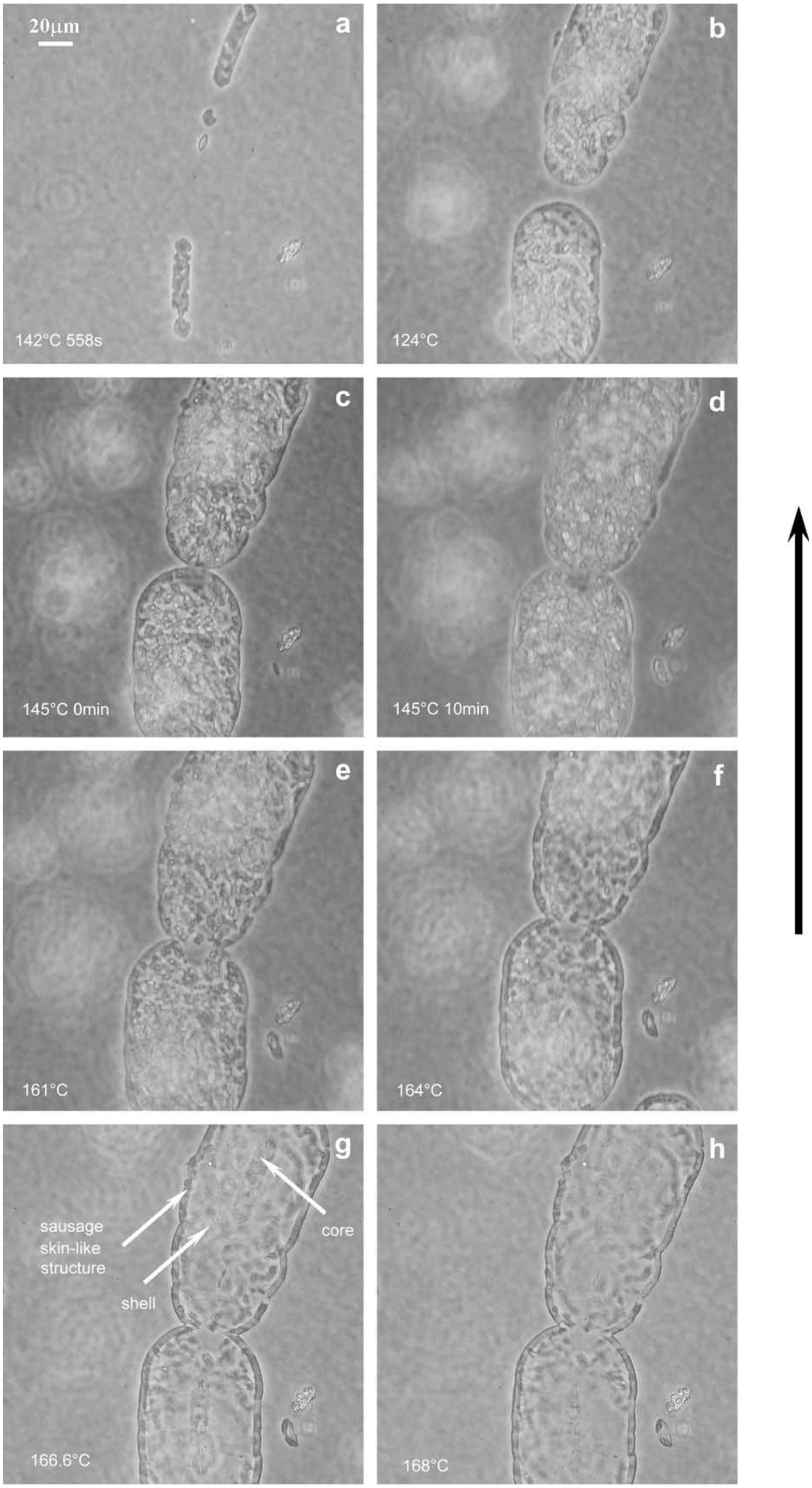


Fig. 5. Phase contrast micrographs of iPP/HDPE = 50/50 sheared samples. iPP/HDPE = 50/50 samples were sheared at 142 °C with shear rate 1.5 s^{-1} and shear time 10 s, and isothermally crystallized at 142 °C for 10 min (a), then the temperature was decreased to 124 °C at the rate of 5 °C/min (b). As soon as it reached 124 °C, the temperature was increased to 145 °C at the rate of 30 °C/min (c) and held for 10 min (d). Finally, the temperature was elevated to 170 °C at the rate of 2 °C/min: (e) taken at 161 °C in the melting procedure to 170 °C; (f) taken at 164 °C in the melting procedure; (g) taken at 166.6 °C in the melting procedure; (h) taken at 168 °C in the melting procedure. The arrowhead represents shear direction.

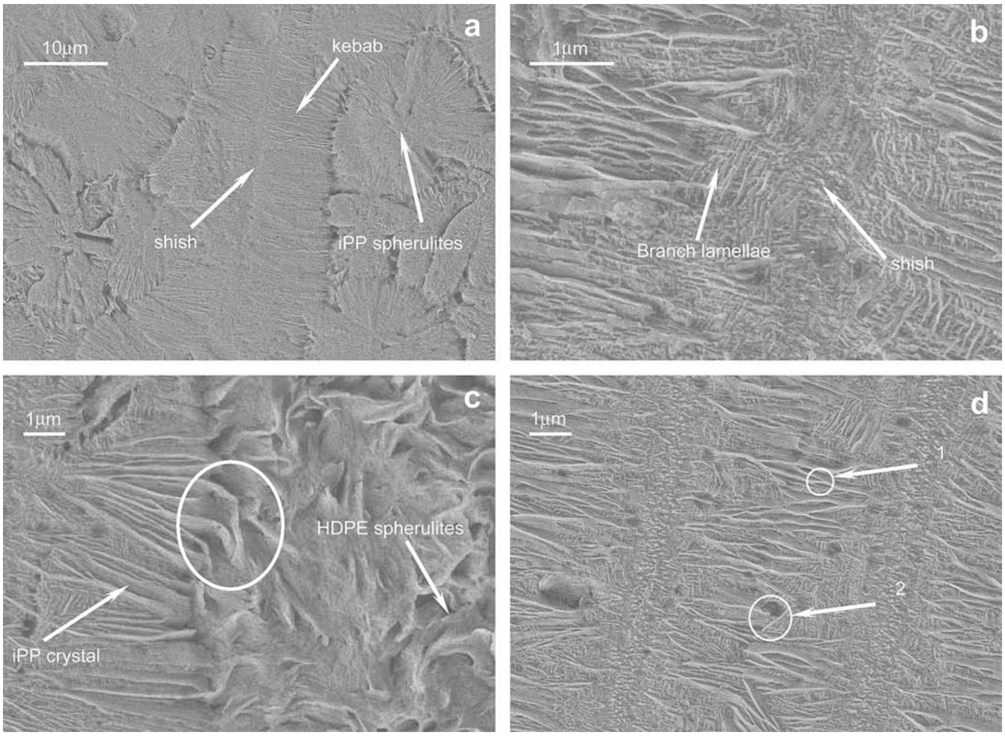


Fig. 6. SEM micrographs of the etched iPP/HDPE = 50/50 sample after sheared at 142 °C with shear rate 6 s^{-1} and shear time 30 s, and isothermally crystallized at 142 °C for 31 min. Then decreased to 123 °C at the rate of 5 °C/min for 5 min: (a) and (b) iPP shish–kebab morphology in iPP rich domains; (c) the interface of iPP/HDPE crystals and (d) two neighboring iPP cylindrites. The arrowhead represents shear direction.

shown in Fig. 6(d). Hobbs and coworkers studied shish–kebab of polyethylene (PE) by atomic force microscopy (AFM) [10], and suggested three different possibilities of interdigitation of PE shish–kebabs. The first kind is that two lamellae miss each other and pass by without having to change directions. The second kind is that they can hit each other and therefore stop growing. The third kind is that they can change their direction so as to avoid hitting each other. In our system, the interdigitation and overlap of iPP kebabs can also be observed. Fig. 6(d) displays two ways of interdigitation of iPP lamellae. One is that kebabs of adjacent cylindrites impinge

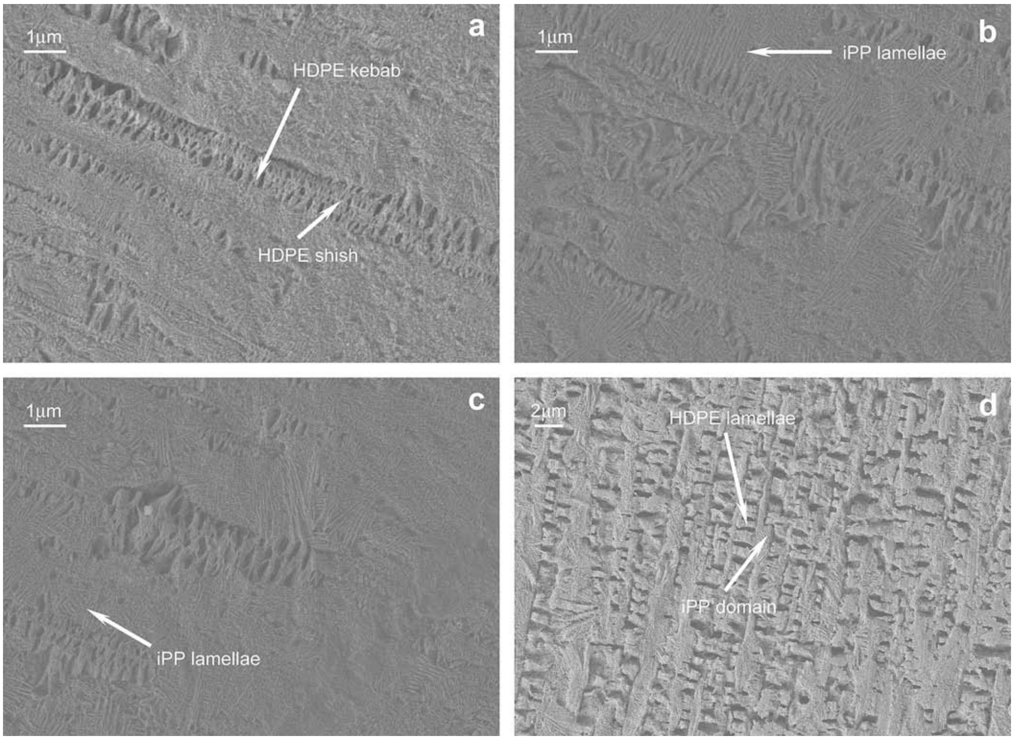
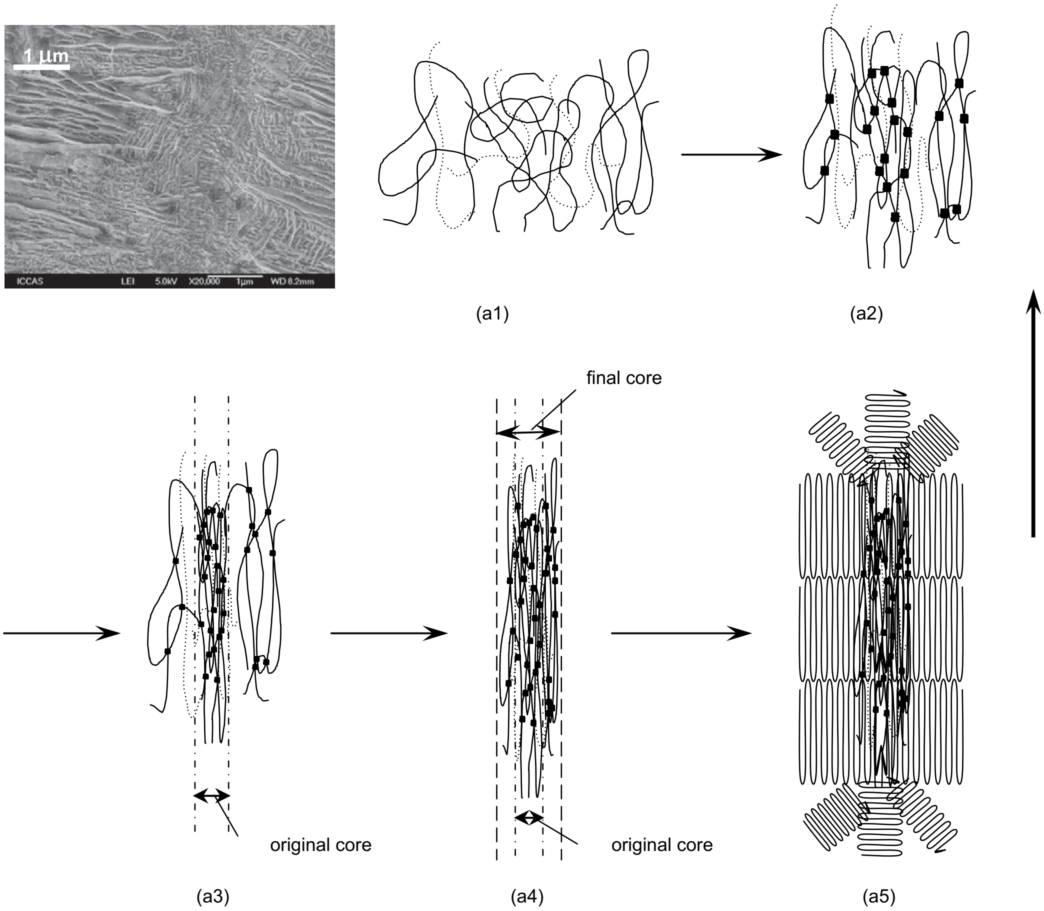


Fig. 7. SEM micrographs of the etched iPP/HDPE = 50/50 sample after sheared at 142 °C with shear rate 6 s^{-1} and shear time 60 s, and isothermally crystallized at 142 °C for 31 min. Then decreased to 123 °C at the rate of 5 °C/min for 5 min. (a)–(c) HDPE shish–kebab morphology in HDPE rich domains; (d) transcrystalline like morphology.

into each other and then stop lateral growth (pointed out by white circle 1). The other is that they miss each other and continue their growth (by white circle 2).

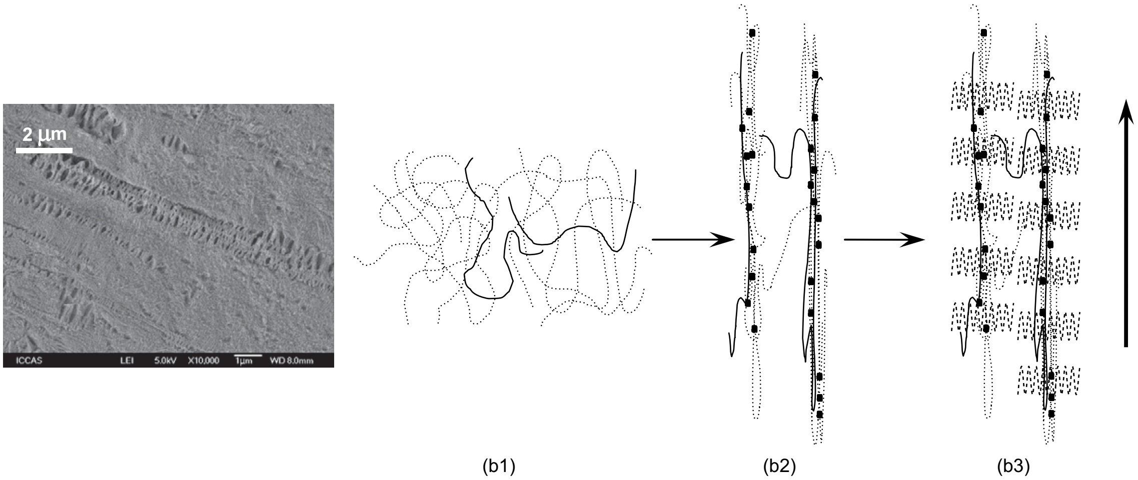
Fig. 7 is the SEM pictures of some shish–kebab like structures from iPP/HDPE = 50/50 blend in HDPE rich domain. In Fig. 7(a), two arrows indicate shish and kebabs separately. Shish aligns along the shear direction, while highly ordered lamellae (kebabs) grow perpendicularly to the shish. This morphology resembles that of HDPE shish–kebabs obtained in subskin zone of gas-assisted injection molded HDPE samples [26], shish–kebabs of polyethylene sheared with razor blade [10], and shish–kebabs of UHMWPE sheared with Linkam CSS-450 shear hot stage [30]. In addition, the width of this kind of shish–kebab (the whole cylindrite) is about 1 μm, which is in consistent with that of pure HDPE shish–kebab in Fig. 2(B).

Comparing Fig. 6(b) with Fig. 7(a), it could be seen that the width of HDPE shish core is about 100 nm, which is smaller than that of iPP shish (1–2 μm). This phenomenon may be explained as follows.



(a1) (a2) (a3) (a4) (a5)

(a) iPP shish kebab in iPP rich domain



(b1) (b2) (b3)

(b) HDPE shish-kebab in HDPE rich domain

Fig. 8. The schematic representation of the formation of shear-induced cylindritic crystallization in iPP/HDPE = 50/50 blend. The solid line and broken line represent iPP chains and HDPE chains, respectively. The black arrowhead represents shear direction.

First, the molecular weight of HDPE is lower than that of iPP and the polydispersity of HDPE is higher than that of iPP. So the degree of entanglement of HDPE polymer chains is lower than that of iPP chains due to the short chain fractions of the HDPE in the system. Second, HDPE has fewer numbers of side chain branching compared to iPP which has a methyl side group per monomer, the interaction force between HDPE polymer chains is lower than that of iPP. Meanwhile, HDPE chains are more flexible than iPP chains, and the HDPE network strands are easier to be stretched after shear. But at the same shear condition, the stretched and oriented network strands more easily relax into isotropic state due to higher flexibility and lower steric interactions of HDPE chains. Finally, since the annealing temperature is 142 °C which is below the equilibrium melting point of polyethylene, the shear-induced deformation of HDPE may have already started some nucleation processes. And when the temperature is lowered to 123 °C, further nucleation and crystallization may go rapidly. Consequently, the shish of HDPE do not have enough time to develop into big size. Meanwhile, the nucleation and growth rate of iPP are lower than that of HDPE and partially aligned polymer chains around the entanglement point may form nuclei and become very small crystallites. These will enhance the network deformation through the crystalline cross-linking sites and promote further deformation and crystallization to form a wide (1–2 μm) and long "shish" like core of the iPP cylindrite. Due to this small nucleation density, the iPP shish can involve more network strands and cross-links and consequently forms wider cylindrite core (shish) and then grows into much wider cylindrite. Besides HDPE shish–kebabs, we can also observe many iPP lamellae growing in iPP rich domains, and even extending into the HDPE rich domains as shown in Fig. 7(b) and (c).

Friedrich and coworkers [31] studied microfibrillar reinforced composites comprising low density polyethylene (LDPE) and microfibrils of poly(ethylene terephthalate) (PET). It was observed in TEM micrographs that LDPE transcrystalline layers were aligned perpendicular to the surface of PET fibril.

In our system, similar morphology is observed. iPP rich domains are elongated and oriented along the shear direction, and fibril-like phase domain structures are formed by shear. Highly ordered HDPE lamellar-transcrystalline like layers stack between these iPP domains. First, after shear, two-phase domains are stretched and oriented. During the time (31 min) that the sample is isothermally crystallized at 142 °C, nucleation and crystallization have happened in iPP rich phase domains. When the temperature drops to 123 °C, the oriented iPP rich domains are filled with iPP crystals including spherulites and even shish–kebab structures, which make an iPP rich domain just like an elongated crystal or a cylindrite. Then HDPE polymer chains were induced to crystallize heterogeneously around the iPP rich domain using the domain walls as the nucleation sites. Second, as HDPE shish are very thin [22], perhaps they have been washed off during the long etching time, and consequently not observed.

3.5. Mechanism of shish–kebab structure in iPP/HDPE blend

Based on our observations of optical micrographs and SEM micrographs, the growth and morphology of shish–kebabs are depicted in Fig. 8. Fig. 8(a) illustrates iPP shish–kebab in iPP rich domains. The interlinking lamellae in both shish and kebab structures are omitted for the sake of clarity. Fig. 8(b) shows formation process of HDPE shish–kebab structure in HDPE rich domains.

Fig. 8(a1) and (b1) depicts that the network chains are entangled and in the random coil conformation before shear. Some HDPE chains are incorporated in iPP rich domains, while some iPP chains are also incorporated in HDPE rich domains (the solid line represents iPP chain and the broken line represents HDPE chain). In Fig. 8(a2), at original stage of shear process, the entangled network chains are stretched and oriented slightly. Only aligned polymer segments concentrated around the entanglement points have a better chance to be nucleated and form crystallites (these crystallites are showed with small black block). As the time is prolonged during shear, the stretched and entangled network chains become slim, and crystallize more, then form the original iPP shish core and other network chains around it are also stretched by shear as shown in Fig. 8(a3). Fig. 8(a4) displays some slim elongated and stretched network structures including partially aligned crystallites merge together and probably absorb other iPP chains around them during shear and then form the long and wide shish nuclei of iPP (final iPP shish core). In Fig. 8(b2), HDPE shish core is formed as soon as the little crystallites are created and the entangled network is stretched to some extent because HDPE has very rapid nucleation and growth rate. Fig. 8(a5) and (b3) depicts shish–kebab morphology in the blend. Stacks of lamellae grow perpendicularly to the shear direction, and two kinds of shish–kebabs are formed.

4. Conclusions

In this study, two kinds of shish–kebab structures were observed in phase-separated iPP/HDPE blend. Both iPP shish–kebabs in iPP rich domains and HDPE shish–kebabs in HDPE rich domains can be formed at low shear rate. At the low shear rates used in our experimental conditions, the entangled network structures cannot be pulled-out and disentangled, which means that the shish are formed by the oriented, stretched and entangled network strands instead of pulled-out chains. Then the lamellae grow perpendicular to the shish through secondary nucleation and finally the shish–kebab structures are formed in this binary blend system.

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